ETHANOLYSIS OF PENTA- AND TETRAMETHYLDISILOXANE CATALYZED BY AQUEOUS HYDROCHLORIC ACID

J. J. Tondeur, G. Vandendunghen and M. Xhigne

University of Mons, B-7000 Mons, Belgium

Received September 14, 1976
Accepted September 29, 1976

The rates of cleavage of the Si-H bond of penta- and tetramethyldisiloxane have been studied. The reaction is first order in the silane and in the dilute acid. However, at high acid concentrations, the rate of reaction is governed by the acidity function of the system: this may indicate fast reversible proton transfer from the solvent to the organosilane in the rate-determining step.

INTRODUCTION

The acid-catalyzed solvolysis of organosilanes has been described with reference to the rate equation, the role of polar substituents and the solvent isotope effect. The main observations were as follows:

(a) The reaction is first order in oxonium ion at acid concentrations below 0.5 mol/l in aqueous ethanol /1/.

(b) Electron supply, which makes silicon more negative in the transition state than in the ground state, slightly facilitates the reaction. The first order constants were correlated using the Taft equation /2/.

(c) An O-H bond is broken in the rate-determining step /3/.

In this paper, a study is reported on the acid-catalyzed ethanolysis of mono- and diorganosilicon hydrides containing a siloxane bond.
Pentamethyl- (Si$_2$H) and tetramethyldisiloxane (Si$_2$H$_2$), obtained by the method of Chvalovsky /4/, were distilled on a spinning band column and the purity of the fractions was checked by gas chromatography. The catalyst was dry hydrogen chloride dissolved in a water-ethanol mixture as required and the reaction was followed by means of a thermostated gas burette. The acidity function H was determined by Braude's method /5/, p-nitroaniline being used as indicator. IR of reaction product: SiOC$_2$H$_6$ vibrations at 1170, 1100, 950 and 810 cm$^{-1}$.

**CALCULATIONS**

**Pentamethyldisiloxane.** From the constancy of the halflife and the slope of the log(C$_{\text{Si}_2\text{H}_2,0} - C_{\text{Si}_2\text{H}_2}$) versus time straight lines we conclude a first order in the hydride.

The pseudo-first order rate constant $k_1^I$ (Table 1) is not proportional to the acid concentration, however, a rough correlation exists with $C_{\text{HCl}}^2$.

**Tetramethyldisiloxane.** The reaction is first order in Si$_2$H$_2$, as can be verified from the initial rates. The hydrogen evolution vs. time curves were approximated with a two-step mechanism. The best results are obtained when $k_1^I$ is equal to 2$k_2^I$, therefore, the kinetic law is $C_{\text{H}_2} = C_{\text{Si}_2\text{H}_2,0} (2 - 2e^{-k_2^I t})$.

**DISCUSSION AND CONCLUSIONS**

The kinetic constant $k_2^I$ is nearly equal to $k_1^I$, meaning that both SiH functions are independent in tetramethyldisiloxane. As can be calculated from the data of the Table, the order in acid varies with the concentration. A mechanism implying second order in HCl is hardly conceivable owing to the poor catalytic activity of undissociated HCl and the weak nucleophilic character of Cl$^-$.  

102